

J. BILLITZER.
 PROCESS FOR THE ELECTROLYSIS OF ALKALI CHLORIDS.
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928,734.

Patented July 20, 1909.

Fig. 1

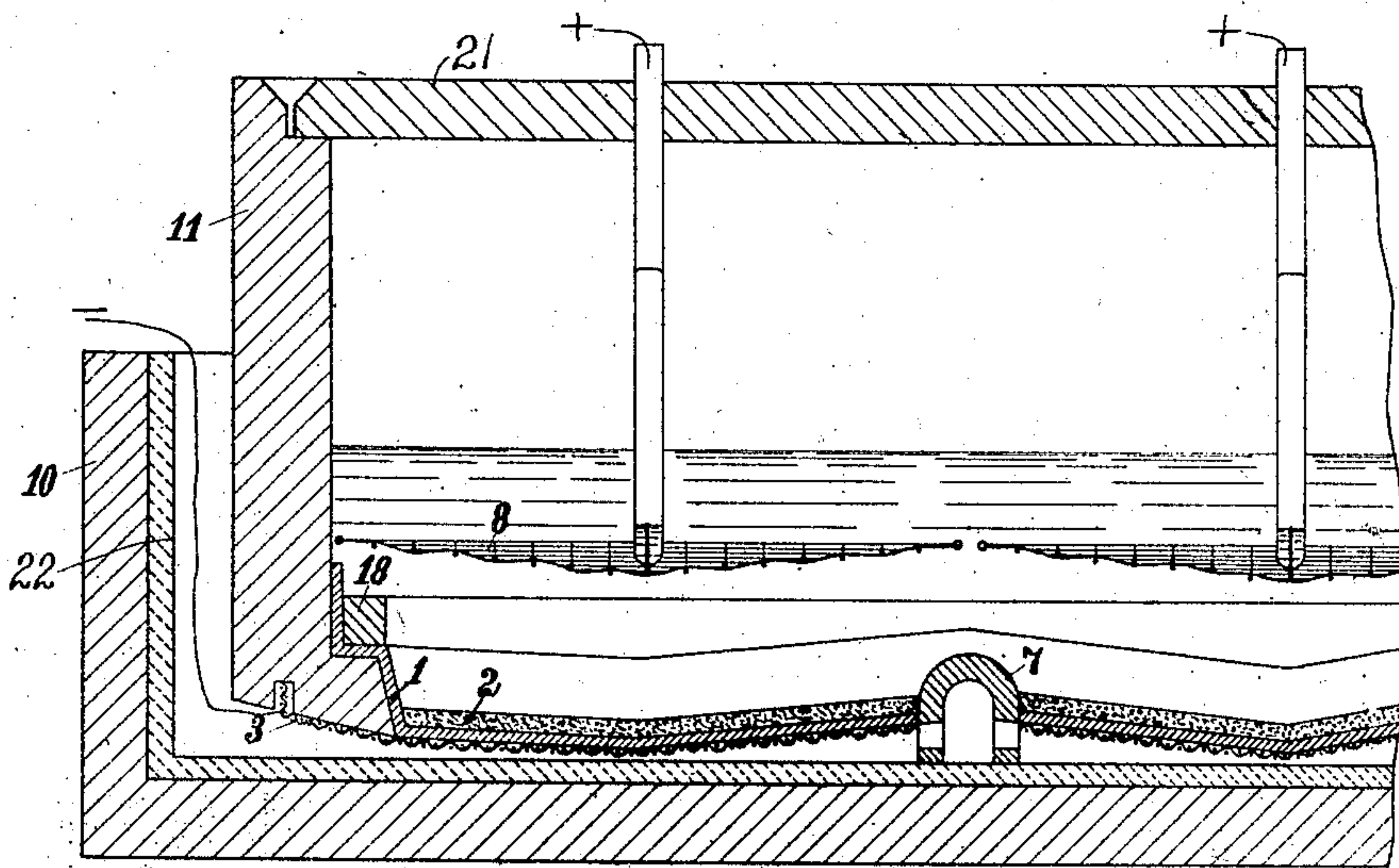


Fig. 2

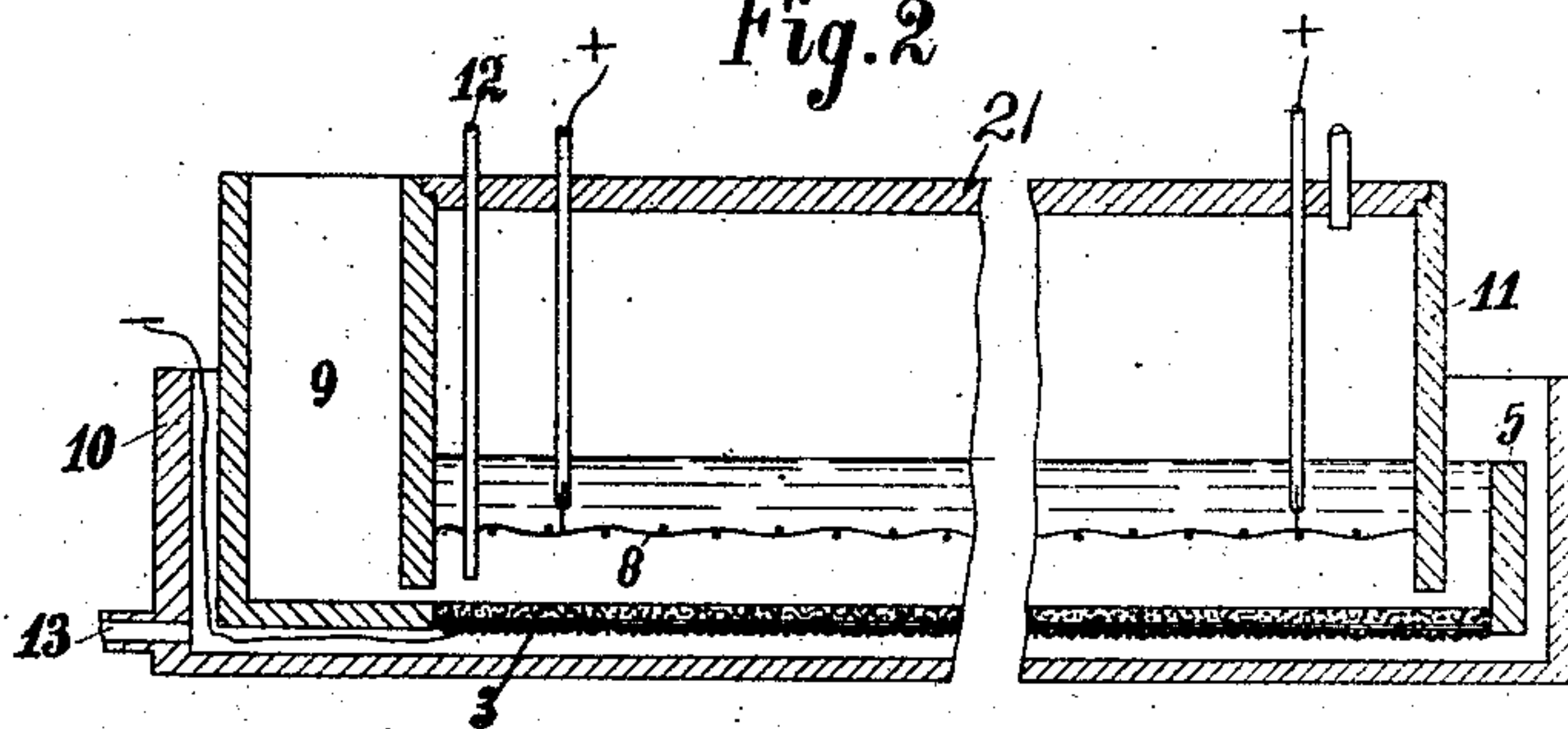
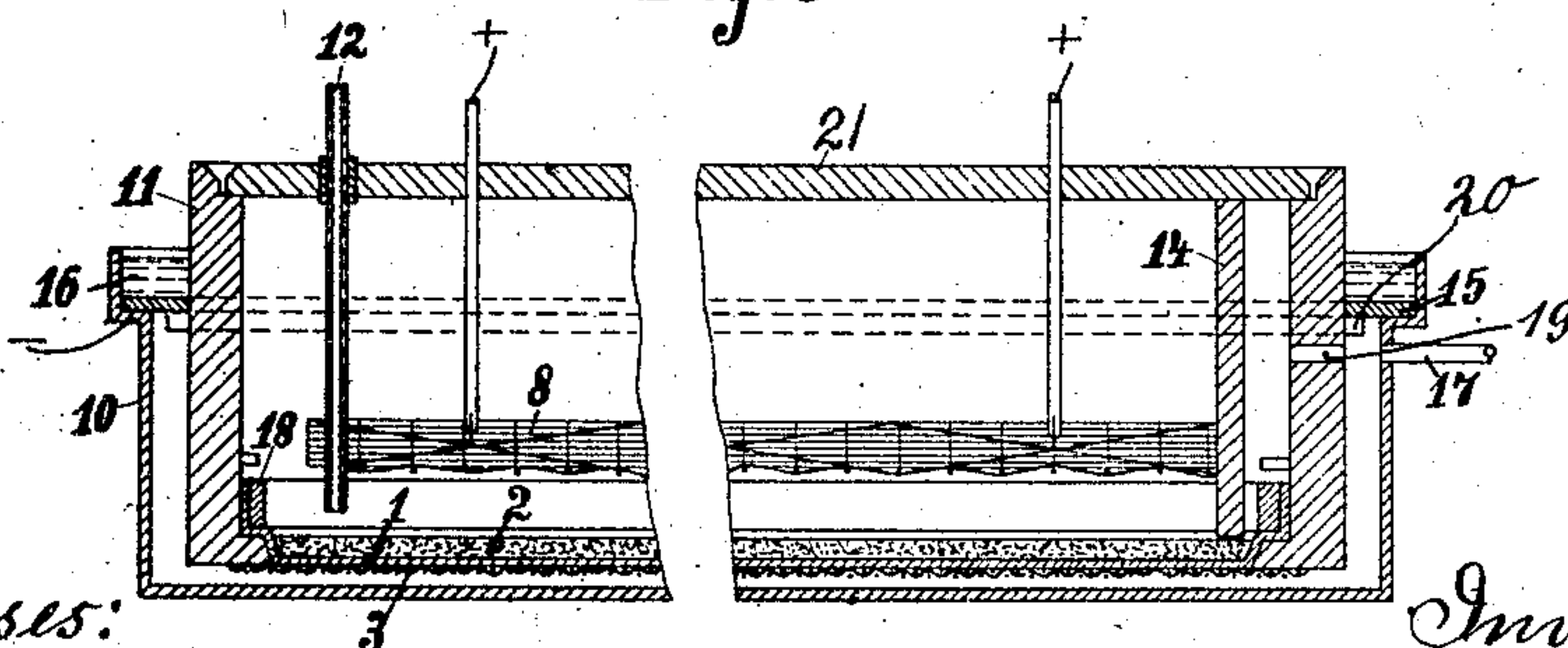


Fig. 3



Witnesses:

Octavius Knight
 H. Alfred J. J. J.

Inventor:

Jean Billitzer
 by *[Signature]*
[Signature]

UNITED STATES PATENT OFFICE.

JEAN BILLITZER, OF VIENNA, AUSTRIA-HUNGARY.

PROCESS FOR THE ELECTROLYSIS OF ALKALI CHLORIDS.

No. 928,734.

Specification of Letters Patent.

Patented July 20, 1909.

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To all whom it may concern:

Be it known that I, JEAN BILLITZER, chemist, a subject of the Emperor of Austria-Hungary, residing at Reiserstrasse 21, Vienna, III, Austria-Hungary, have invented certain new and useful Improvements in Processes for the Electrolysis of Alkali Chlorids, of which the following is a full, clear, and exact description.

It is well known that difficulty is encountered in obtaining chlorin and fairly concentrated soda lye from chlorid of sodium solutions, by means of the electric current and cheap and simple apparatus of good current efficiency. The types of mercury apparatus, though operating satisfactorily, are very expensive, complicated and require careful attention.

The bell apparatus while giving a comparatively good yield, requires a high tension during the electrolysis and does not yield concentrated lyes.

In order to obtain a good yield of concentrated lye applicant has devised a new process. This process though principally designed for the chlorid of sodium electrolysis may be also employed without any difficulty in all cases in which through the action of the electric current upon a solution a gaseous and a liquid product is formed.

The idea involved in this process is shortly as follows: In a suitably arranged apparatus, the anodes are disposed above the substantially horizontal cathodes with a diaphragm also substantially horizontally between them. Between the anodes and this diaphragm a formation of layers is produced by means of the electrolysis, which renders the solution weaker. This will diminish the density of the anode solution, while the portion of the solution next to the cathode and immediately above the diaphragm will increase its specific weight and thus gravitate as a layer next to the diaphragm. Since layers of liquids at rest cannot be kept for any length of time from diffusing into each other, the two solutions thus produced are separated by supplying fresh salt solution from above and by compelling the lower heavier layer to flow through a slot, disposed near the diaphragm and extending over the whole width of the latter, and by arranging a dam behind this slot. By these means the heavier layer will be constantly removed as it is

formed. In order to obtain stationary conditions the supply of fresh salt solution and the current intensity have to be chosen so that when the formation of layers has once commenced as many chlorin ions go to the anode as can escape from it. In order to facilitate the formation of layers the lower layer described may be brought into contact with undissolved sodium chlorid in order to remain always saturated. In order to facilitate this formation and regeneration of layers a new and particularly suitable diaphragm is used, which, though described and shown in this application to make fully clear my novel process, forms the subject-matter of a divisional application Serial No. 438,981, filed June 17th, 1908. This diaphragm has, aside from its many other advantages, the particular features of having an accurately regulatable permeability and of adapting itself well to the form of the cathode, so that the separation aside from being produced by the formation of layers, is further aided by the inner hydrostatic pressure. Furthermore, through the rewetting of the cathode by means of the solution running off, the contact is kept permanent and the running off of the soda lye insured.

According to applicant's method above described has the separation into layers of small quantities of liquid been rendered possible, and this only by having the separating layer thin by causing same to renew itself automatically during the process of electrolysis and by forcing it to form a distinct separating layer. Only by this arrangement it has been made possible to completely separate anode and cathode products, obtaining at the same time comparatively concentrated solutions of soda lye, that is, solutions of from ten to twenty per cent.

In order to make clear the invention, the process will be described in detail in the following with the aid of the accompanying drawings which show diagrammatically an apparatus used for this process.

In these drawings Figure 1 is a part of a longitudinal section of the apparatus; Fig. 2 is a transverse section of same; Fig. 3 is a longitudinal section of a modification of the apparatus.

The apparatus shown in Figs. 1 and 2 comprises a bell 11, which is closed at its

lower end by means of a diaphragm 1, 2, resting upon a wire net 3 of iron, nickel or other suitable material, which serves as the negative electrode. The entire bell is suitably supported and disposed within a trough 10. Within bell 11 is arranged anode 8 of platinum, carbon or other suitable material in parallel to and at a small distance from the cathode net 3.

In manufacturing the apparatus various materials may be employed. Plates of glass, wire-glass or pottery may be used, which are embedded in cement or in asphalt, as shown, for instance, in Fig. 1 at 22, or reinforced concrete or stone plates may be used.

In order to obtain a complete separation of the electrolytic products (soda lye and chlorin) the process is carried out in the following manner: The bell 11 is supplied with the electrolyte to a certain height, trough 10 being empty at the beginning of the process. The diaphragm being permeable for liquids will allow the salt solution to percolate through to the cathode where soda lye is formed. The discharge opening 13 for the lye is disposed so that the liquid passing into trough 10 will attain a suitable height to just wet the cathode net.

In order to facilitate the escape of the hydrogen bubbles produced on the cathode during the electrolysis the cathode may be suitably shaped for instance by arranging the net in wave form (Fig. 1) with its highest portions abutting against channel 7 formed of impermeable material, through which the gas can easily escape, or by placing the plane or corrugated cathode net altogether slightly slantingly; an incline of 1:20 would be sufficient to cause the hydrogen to wander toward the higher portion of the net. A satisfactory operation of this arrangement however is only possible by using a suitable kind of diaphragm. It is essential to use diaphragms, the permeability of which for liquids is accurately regulatable without offering great electrical resistance, and which adapt themselves well to the form of cathode. All diaphragms which are not pliable such as carborundum, cement, sheet asbestos and the like are not suited for this purpose. Pulverized diaphragms are not suited either, since they are not plastic and are not permanent.

Applicant has succeeded in designing a new diaphragm by covering the net cathode 3 with ordinary commercial asbestos cloth 1 (Fig. 1) and putting on same a pulverized diaphragm 2 of a particular kind. The pulverized diaphragms heretofore known are not suited for inclined surfaces, owing to the powder soon shifting down the incline. Besides these diaphragms have the disadvantage of cementing and thus soon becoming impermeable; for this latter reason they

cannot be used for this purpose even in connection with fixed ribs, which prevent the sliding of the powder. Both of said disadvantages have been overcome by applicant by using a diaphragm body consisting of a mixture of insoluble powders, such as sulfate of barium, clay or the like, and asbestos-wool, which mixture is formed in sodium chlorid solutions into a plastic but still tough and resistive mass. Mixtures of suitable powders with asbestos wool can be made very quickly and very easily. While for instance sulfate of barium alone requires several hours to deposit, a suspended mixture of pulverized sulfate of barium and asbestos-wool deposits in a twenty (20%) per cent. sodium chlorid solution in a few minutes. This deposit being at first tough, may be easily dried, whereby it may be formed into any shape, which it retains during its further use for a long time even in liquids.

These diaphragms are extremely strong and may be used for months and years and furthermore they can be exchanged or renewed very quickly and easily, contrary to ordinary powder diaphragms. It is only necessary to renew the asbestos-wool powder layer or to exchange the whole diaphragm by lifting out the asbestos cloth with the layer. This operation requires only a few minutes. These diaphragms dry and harden in the air completely after some time, but regain their pliability and permeability when placed for a short time in water or in a solution of any suitable kind.

By varying the proportion of asbestos-wool and sulfate of barium or clay powder, as well as by varying the thickness of the layer, the permeability of the diaphragm may be regulated at will.

Applicant uses for producing lyes of from eight to thirteen per cent. on a diaphragm surface of one hundred square centimeters, a mixture of one hundred and ninety grams Ba SO_4 with from three to six grams asbestos wool; for producing thirteen to eighteen per cent. lyes, two hundred and seventy-five grams Ba SO_4 with from 8 to 10 grams asbestos-wool; for obtaining still more concentrated lyes, 350 grams of Ba SO_4 with 15 grams of asbestos-wool.

During the electrolysis in the apparatus described above soda lye is formed in trough 10 while the chlorin ions wander to the anode where they are discharged and escape as gaseous chlorin. Fresh salt solution is supplied through feeding pipe 12 (Fig. 2) which runs into the solution close to the diaphragm. Therefore the upper portion of the salt solution will be weakened in salt during the electrolysis while the lower portion will increase its density so that owing to the different densities of the two portions, a distinct layer is formed immediately above the diaphragm. In order to further facilitate

tate the formation of the layer a chamber or pocket 9 (Fig. 2) of impermeable material may be provided in the bell, which is supplied with cooking salt, and which communicates near the bottom with the electrolysis chamber, so that the layer resting directly upon the diaphragm is constantly saturated with cooking salt and therefore its specific weight rendered still greater. This latter precaution is particularly advisable when the fresh solution is supplied very slowly in order to obtain very concentrated lyes. In this case the solution would grow too weak in salt without the pocket above referred to.

During the electrolysis the solution not only reaches the cathode through the diaphragm, but is also forced to run over a dam 5 (Fig. 2) in order to wet the cathode from below. Instead of using a dam, a baffle plate 14 (Fig. 3) may be provided within bell 11 having its opening near the diaphragm. The pocket, thus formed by this plate, communicates with the trough 10 through an outlet 19 provided at a suitable height. By this arrangement shown in the two modifications the irregularities of supply of solution or of the permeability of the diaphragm are equalized on one hand, on the other hand, this being the most essential point, this arrangement has the following particular advantage: During the passing of OH ions to the anode, or owing to insufficient action of the diaphragm, soda lye is apt to reach the lower layer of the liquid, which in the further course of electrolysis forms with the chlorin, hypochlorite, which latter would cause disturbances in the process and decrease the output. By compelling the solution contained in the bell to constantly flow over the dam any trace of soda lye, which may have diffused into the bell, is washed out immediately since according to the arrangement described above, just the lowermost layers next to the diaphragm are compelled to flow over the dam.

As mentioned already the liquid level is kept in the trough preferably high enough to wet the cathode net, which however is not absolutely necessary, as the liquid level may also be rather below the level of the cathode, because owing to the filtrating of the solution through the diaphragm and owing to the liquid flowing over the dam the cathode net is permanently wetted with liquid. (On account of clearness the space between dam 5 and bell 11 is shown in Fig. 2 much wider in proportion than it is in the practical apparatus where this space is chosen as narrow as possible, in order to avoid diffusion.)

The apparatus has been subjected to several uninterrupted electrolysis tests, each lasting six weeks and yielding at from four to five volt tension during the time of the electrolysis an average output of twelve per cent. lye, being equal to from ninety to ninety-

five per cent., (rarely eighty-five to ninety per cent.) of the theoretical output, while at the same time substantially chemically pure chlorin of ninety-nine per cent. was obtained.

No difficulty is encountered in obtaining an output of from ten to fifteen per cent. and even more concentrated soda lye. An apparatus having a cathode net of one square meter surface consumes at a tension of from 4 to 4.5 volts and a temperature of 60° C., about 600 amperes.

In smaller apparatus (up to 100 amperes capacity) it is more advantageous to fix the asbestos cloth to the bell. The whole bell, together with the diaphragm may then be placed upon a corrugated wire net of sufficient strength corresponding in form with the bottom of the outer trough and resting thereon. The trough 10 may be made to advantage of sheet iron, which serves in this instance at the same time as a part of the electric circuit.

For larger apparatus (consuming more than 100 amperes) the structure above referred to is not suited. In apparatus of that size it is more practical to have the cathode net fixed to the bell.

In order to facilitate the exchanging of the diaphragm without renewing the bell, the cover 21 of the latter and the baffle plate 14 are made easily removable (Fig. 3). The asbestos cloth is not fixed to the bell but is held in place by means of a frame 18 of stone or other suitable material, running on the inside of the trough and held in place by means of wedges. For tightening the frame against leakage if necessary a non-soluble powder may be used. Upon the asbestos cloth is then placed the asbestos powder mixture. For the purpose of renewing the diaphragm it is only necessary to remove the bell cover, the baffle plate and the frame, whereafter the diaphragm may be exchanged in a few minutes.

In Fig. 3 is shown an apparatus by means of which it is also possible to collect the hydrogen separately. For this purpose a tight fitting frame 15 running on the outside of bell 11 is resting upon a rim 20 provided on the bell and upon the upper rim of trough 10 which is suitably shaped for this purpose as shown in Fig. 3. The channel thus formed by the bell, the trough edge and frame 15 may be filled with a liquid of suitable kind to further tighten the frame against leakage of gas.

The pressure at which the hydrogen is discharged through the opening 17 may be easily regulated by regulating the liquid level at the discharge opening 13.

The hydrogen may be either utilized as such or may be used with the chlorin generated during the electrolysis for directly producing chemically pure hydro-chloric acid

by means of a blow pipe similar to the oxygen hydrogen blow pipe.

In order to free the hydrogen of the atomized soda lye carried along by same while rising, it must of course pass through a long tube or over a body of large surface before it can be used in connection with chlorine as above mentioned.

While I have described and shown various forms of the apparatus by means of which my novel process is carried out, I do not claim the particular novel features of these forms of the apparatus, since they form the subject-matter of a divisional application.

What I claim is:

1. The hereinbefore described process for electrolysis of alkali chlorids, comprising the compelling a part of the cathode product to form a thin layer in the electrolyte and the constant removal of said layer as it is formed.

2. The hereinbefore described process for electrolysis of alkali chlorids, comprising the compelling a part of the cathode product to form a thin layer in the electrolyte and the constant removal of said layer as it is formed through an opening of suitable size disposed at the height at which said layer is formed.

3. The hereinbefore described process for electrolysis of alkali chlorids, comprising the compelling a part of the cathode product to form a thin layer in the electrolyte and the constant removal of said layer as it is formed through an opening of suitable size disposed at the height at which said layer is

formed by constantly adding fresh solution to the electrolyte.

4. The hereinbefore described process for electrolysis of alkali chlorids, comprising the compelling a part of the cathode product to form a thin alkali-containing layer of higher specific gravity immediately above a diaphragm, and the constant removal of only said layer from above the diaphragm through an opening of suitable size disposed at the height at which said layer is formed by constantly adding fresh solution to the electrolyte.

5. The hereinbefore described process for electrolysis of alkali chlorids, comprising the compelling a part of the cathode product to form a thin alkali-containing layer of higher specific gravity immediately above a diaphragm, and the constant removal of only said layer from above the diaphragm through an opening of suitable size disposed at the height at which said layer is formed and also comprising the removal of said layer by percolation through said diaphragm by constantly adding fresh solution to the electrolyte, the re-diffusion of the electrolyte collecting underneath the cathode being prevented by preventing the electrolyte from rising above the level of the cathode.

In witness whereof, I hereunto subscribe my name this 10th day of January A. D. 1907.

JEAN BILLITZER.

Witnesses:

WOLDEMAR HAUPT,
HENRY HASPER.